"TEFLON" FLUOROCARBON RESINS— SAFETY IN HANDLING AND USE

DUPONT
REG. U.S. PAT. & TM. OFF.

There's a world of things we're doing something about.

Produced by Saint-Gobain Performance Plastics Inc.

Exhibit 006

TABLE OF CONTENTS

"Teflon" is Du Pont's registered trademark for its family of fluorocarbon resins, fibers, and film, including TFE (tetrafluoroethylene) resins and FEP (fluorinated ethylene propylene) resins.

"TEFLON" FLUOROCARBON RESINS— SAFETY IN HANDLING AND USE

"Teflon fluorocarbon resins, due to their unique combinations of physical, electrical and chemical properties, have found application in nearly every field of modern industrial, technological, and scientific endeavor. In addition, they have found such extensive use in domestic cookware and home shop applications that the trademark "Teflon" is widely recognized by the consuming public.

Structurally, there are two general types of "Teflon" resins. "Teflon" TFE resin is a polymer consisting of recurring tetrafluoroethylene monomer units whose formula is $-(CF_2 - CF_2)\overline{n}$. "Teflon" FEP resin is a copolymer of tetrafluoroethylene and hexafluoropropylene with the formula $-(CFCF_3 - CF_2 - (CF_2 - CF_2)n)\overline{m}$.

This booklet has been written to provide guidelines for the safe handling and use of these products in a wide variety of situations. These include varying temperatures, skin contact, ingestion, scrap disposal, machining, fire safety, reactivity toward certain chemicals, and medical uses.

I. USE AT HIGH TEMPERATURES

Of the many unique properties that characterize "Teflon" fluorocarbon resins, one of the most important is resistance to heat. While few plastics are capable of continuous service much beyond the boiling point of water, "Teflon" resins can withstand the temperatures inside baking ovens and in the engine compartments of modern jet aircraft. Combined with almost total chemical inertness, dielectric stability, and non-flammability, the heat resistance of "Teflon" gives a versatility that is unmatched by any other engineering material.

Specifically, "Teflon" TFE resins are rated for continuous service at 260°C (500°F), while "Teflon" FEP resins are rated at 205°C (400°F). Moreover, "Teflon" resins retain useful strength, flexibility, and dielectric properties over broad ranges of environmental conditions even at temperatures of 350°C (662°F) or higher for short periods of time. Many applications of "Teflon" utilize this ability to serve for limited periods at temperatures above the rated values, e.g., electrical arc-quenching equipment and fire alarm cable, flexible hose, nonlubricated bearings, and other components which may be subject to sudden, great changes in temperature. In such applications, "Teflon" resins are often used to provide the margin of safety needed in the event of fire, electrical overload, and similar emergencies.

While most inorganic engineering materials, such as metals or ceramics, simply soften and lose strength when overheated, plastics and other organic materials in addition undergo some decomposition or actual breakdown in chemical structure. The products thus formed are usually given off in the form of gases or fumes. Almost without exception, the fumes liberated from decomposing organic materials are objectionable from the standpoint of health and safety.

The high temperature ratings of "Teflon" resins result from their extremely low rate of thermal decomposition. Even in cases of severe overheating, the quantity of fumes evolved is minute in comparison with most organic materials. The fumes released, even though small in quantity, warrant some care in situations where exposure of personnel is likely to occur.

Since their discovery, over a hundred million pounds of "Teflon" fluorocarbon resins have been processed at temperatures in excess of 370°C (700°F), and placed in end-use applications, many of which have been at or above the rated use temperatures. In this period, spanning more than twenty-five years, there have been no reported cases of serious injury, prolonged illness, or death resulting from the handling of the resins. This record includes the experience of Du Pont personnel, hundreds of processors, and thousands of end-users who handle the resins every day.

The Du Pont Haskell Laboratory for Toxicology and Industrial Medicine studies hundreds of chemical compounds each year to determine their toxicity potential. Over the years, many hours have been spent there in careful investigation of "Teflon" resins. In addition, Du Pont research laboratories have studied intensively the thermal behavior of "Teflon" resins. A number of other laboratories, including those of United States Department of Health, Education and Welfare, have conducted similar studies related to the safety of these resins. The knowledge gained through these studies is summarized in the sections that follow.

A. Pyrolysis Studies

High-temperature studies of "Teflon" fluorocarbon resins have been aimed at answering two pertinent questions: (1) At what temperature does thermal decomposition begin, and at what rate does it proceed thereafter; and (2) what are the decomposition products thus formed?

Weight Loss Vs. Temperature

In general, "Teflon" resins show complete thermal stability up to about 205°C (400°F). By using the most refined analytical technique, some traces of decomposition products can be detected at temperatures between 205°C (400°F) and 232°C (450°F). Above 232°C weight losses become sufficient to provide a means of expressing decomposition rates.

Table I shows weight-loss rates of "Teflon" TFE and FEP resins through a range of practical use temperatures up to 425°C (800°F). By comparison with most organic materials, the weight loss of "Teflon" resins is extremely small. At 260°C (500°F) it is small enough for TFE resins to be essentially negligible from the standpoint of service life. FEP resins exhibit changes in physical strength after prolonged exposure above 205°C (400°F) which largely account for the lower temperature rating for these products.

Decomposition Products

The thermal decomposition products derived from "Teflon" resins have been studied in considerable detail by Du Pont, [1-5] the United States Public Health Service,[6-11] and others.[12-14]

TABLE I

WEIGHT LOSS AND VENTILATION RECOMMENDATIONS FOR FABRICATED "TEFLON" RESINS ABOVE 230°C

Temperature		Initial Weight Loss, Percent/Hour			Air Recommendations, Cubic Feet per Minute per Lb. Resin		
°C	°F	"Teflon" 7A, 7C, 8, 8A, 9A, 9B TFE Resin	"Teflon" 6, 6C, 30 TFE Resin	"Teflon" 100, 110, 140, 160 FEP Resin	"Teflon" 7A, 7C, 8, 8A, 9A, 9B TFE Resin	"Teflon" 6, 6C, 30 TFE Resin	"Teflon" 100, 110, 140, 160 FEP Resin
230	450	0.00005 to 0.0001	0.0001 to 0.0002	0.0004	0.12	0.50	0.86
260	500	0.0001	0.0006	0.001	0.21	1.3	2.1
290	550	0.0003	0.0015	0.01	0.66	3.5	21
320	600	0.0005	0.0045	0.02	1.2	10	42
340	650	0.0018	0.014	0.08	4.2	33	180
370	700	0.004	0.032	0.3	9	73	650
400	750	0.008	0.08		18	180	
425	800	0.15	0.15		325	325	

NOTE: Air recommendations represent the volume of air to reduce gaseous products to levels found safe through long experience in processing "Teflon" resins.

In *INERT ATMOSPHERES* the resins decompose mainly to gaseous monomers, the basic substances from which the resins are synthesized, together with small amounts of other gases listed below. Thus, TFE resins produce mainly tetrafluoroethylene and the FEP resins a mixture of tetrafluoroethylene and hexafluoropropylene. Tetrafluoroethylene and hexafluoropropylene are relatively low in toxicity.[5] At temperatures between 205°C (400°F) and 425°C (796°F) the remaining portion of decomposition products consists of a relatively non-toxic, incompletely characterized waxy sublimate.[5] At 425°C (796°F) and above, small amounts of the toxic gas, perfluoroisobutylene,[4] have been detected. Free fluorine has never been found among the decomposition products of "Teflon" and its formation is not favored thermodynamically.

When the resin is decomposed *IN AIR*, part of the decomposition products react to form carbonyl fluoride (COF_2).[7] If the air is moist, hydrolysis of COF_2 occurs and hydrogen fluoride (HF) and carbon dioxide (CO_2) are formed.[8] The presence of COF_2 and perfluoroisobutylene have been reported at about 500°C (932°F).[5,7] Up to 450°C (842°F) the principal toxic ingredient is particulate matter.[5] Trace

amounts of HF are liberated as low as 400°C (750°F). Studies conducted by the United States Public Health Service indicate that increasing amounts of fluorocarbon particulate matter are formed in moist air and contain increased amounts of carbonyl groups over those obtained in inert atmospheres.[11]

Above 690°C (1274°F) the decomposition products will burn, but the resin will not support combustion once heat is removed. Combustion products are mainly carbon dioxide and hydrogen fluoride, with small amounts of carbon tetrafluoride.

B. "Teflon and Other Organics at High Temperatures

Extensive tests have been conducted with laboratory animals exposed to fabricated forms of "Teflon" and other common polymers at high temperatures. An example is work in which several kinds of wire constructions were subjected to toxicity studies. In these, approximately 20 grams of sample were heated to temperatures ranging from 250°C (483°F) to 350°C (662°F). Rats were exposed for periods up to four hours to the resultant pyrolysis products carried in an air stream of two liters per minute. The range of temperatures producing lethal exposures to one or more rats after four hours of exposure were:

"Teflon" 5 TFE Resin[5]	400°C	752°F
"Teflon" 6C TFE Resin	400°C	752°F
"Teflon" 100 FEP Resin	350°C	662°F
Silicone Rubber	250-300°C	(482-572°F)
Polychlorotrifluoro-ethylene	200-300°C	(392-572°F)
Polyvinyl chloride	300°C	(572°F)

Although rats exposed for four hours to polyvinyl chloride in these tests did not succumb, clinical response was severe and major pulmonary injury was observed for twelve days after exposure.

In similar tests with cooking surfaces coated with "Teflon" TFE resin, it was found that rats survived four-hour exposures at 250°C (482°F). However, similar exposures at the same temperature were lethal to rats when they inhaled products given off from some common cooking fats and oils. In these exposures, the amount of the fat or oil was approximately that which would normally be used in domestic cooking.

C. Polymer Fume Fever

Exposure to thermal decomposition products of "Teflon" fluorocarbon resins has caused a temporary flu-like condition similar to the metal fume fever (or "foundry man's fever") known for many years.[18] These symptoms, called "polymer fume fever", are the only adverse effects observed in humans to date. The symptoms do not ordinarily occur until several hours after exposure, and pass off within 36 to 48 hours, even in the absence of treatment. Observations indicate that these attacks have no lasting effect and that the effects are not cumulative. When such an attack occurs, it usually follows exposure to vapors evolved from the polymer at very high temperatures, up to 425°C (800°F), used in resin processing operations, or from smoking cigarettes or tobacco contaminated with the polymer.[4] The causative agent in the decomposition products has not been identified.[5,11]

Fumes from the pyrolysis of many resins and elastomers, as well as those from naturally occurring polymers like rubber, coal, silk, and wood, may be toxic. Therefore, the ventilation precautions to be observed when heating "Teflon" resins are similar to those which should be observed when heating such conventional materials.

D. Flammability

"Teflon" fluorocarbon resins are nonflammable and do not propagate flame (ASTM-470 vertical flame test). Decomposition products will burn at temperatures above 690°C (1274°F) but combustion is not self-sustaining since the heat liberated is not sufficient to maintain the polymer at decomposition temperatures. In very hot fires which cause appreciable decomposition of "Teflon", heat is absorbed from the surroundings as heat of decomposition. This property tends to limit the damage to "Teflon" resins in such applications as electrical insulation subject to high thermal transients.

Underwriters Laboratories have classified "Teflon" TFE and FEP fluorocarbon resins as "self-extinguishing, Group I" with respect to fire hazard.

E. Handling Practices

As with most polymers, minute quantities of residual gases which may be harmful diffuse from the resin even at room temperature. Therefore, all resin containers should be opened and used only in well ventilated areas to avoid exposure.

In addition, it is recommended that an "elephant trunk," exhaust hood, or similar positive exhaust system be used to remove off-gases released from hot polymers in the work area. This is in addition to the normal ventilation required.

See Table I for recommended ventilation air flow rates for such an exhaust system.

While most high-temperature applications can be adequately handled by ventilation considerations alone as indicted in Table I, a few warrant further consideration. The paragraphs that follow present a brief discussion of these uses and attempt to answer questions most frequently asked by users of "Teflon" resins.

Machining

Grinding, sawing, and machining of "Teflon" resins are performed routinely in fabricator's shops. In rare instances, temperatures may exceed the recommended values. (See Table II for results of laboratory tests.) But since the quantity of resin thus heated is usually quite small, there is normally no need for extra ventilation. Generally, coolants are recommended in machining to improve production rates and quality, and they will serve to control any tendency toward overheating.

Dust generated by machining is physiologically inert. The American Industrial Hygiene Association[14] suggests 15 mg/m^3 (on a nuisance basis) as a satisfactory control level for airborne dust of "Teflon". It is believed that cases of the flu-like symptoms associated with machining operations have been caused by smoking cigarettes contaminated with the resin. For this reason, it is suggested that tobacco not be used or carried in open packs around machining operations.

TABLE II

MACHINING ROD OF "TEFLON": MAXIMUM TOOL TEMPERATURE WITHOUT COOLANT

	RPM	Feed Rate, In./min.	"Teflon": Tool Temp. °C	"Teflon": Tool Temp. °F	Glass Filled "Teflon"*: Tool Temp. °C	Glass Filled "Teflon"*: Tool Temp. °F
Sharp Tool	500	0.25	63	145	75	167
	1,000	0.75	71	160	88	190
	2,000	4	93	199	108	226
Dull Tool	500	0.25	220	426	185	366
	1,000	0.75	215	418	175	347
	2,000	4	137	278	200	388

*50% glass, by volume

Soldering and Hot-Wire Stripping

Some of the large areas of use of "Teflon" are in electrical insulation for radio and radar equipment, in high-speed computers, and in electrical and electronic industrial equipment. In virtually all of these applications, soldering is a routine fabricating procedure. The use of a heated element to remove insulation from wire and cable has also become a routine operation.

As in most uses of "Teflon" resins, the combined effect of temperature, quantity of resin, exposure time, and ventilation conditions during soldering and hot-wire stripping rarely produce conditions of toxicological significance. Any special practices that may be warranted will follow the same common-sense rules applicable to any soldering jobs. For example, prolonged soldering work in confined spaces where natural air circulation is restricted will require some mechanical ventilation for worker comfort; the same is true for shop areas where a number of workers are engaged in soldering or hot-wire stripping operations. Normal ventilation provided for worker comfort usually provides adequate safety for these operations. As an added measure during hot-wire stripping, some shops employ a small exhaust duct at the work bench.

Perhaps the best support for the safe use of "Teflon" resins in electrical and electronic applications is offered by the record of experience to date: though literally millions of pounds of the resins have gone into these uses, there have never been any cases of ill effects reported during soldering or hot-wire stripping of "Teflon" fluorocarbon resins.

Welding and Flame Cutting

Direct application of welding arcs and torches can quickly destroy the usefulness of parts made from most plastics, including "Teflon" resins. For practical reasons, therefore, it is necessary to remove all such parts from equipment to be welded. Where removal is not possible, such as in welding or cutting coated parts, mechanical ventilation should be provided.

Because "Teflon" resins are rated at very high temperatures, parts made from them can survive at locations much closer to the point of direct flame contact, and thus lend themselves to certain in-place welding operations. From an engineering standpoint, it is usually advisable not to heat the TFE resin above its gel point (330°C, 620°F) nor the FEP resin above its rated service temperature (205°C, 400°F). Since the quantity of resin heated in such operations is usually relatively small (less than one pound), ventilation requirements seldom exceed those required for normal welding work. Owing to the possibility of inadvertent overheating, however, the use of a small fan or elephant-trunk exhaust may be advisable.

Scrap Disposal

Disposal of scrap "Teflon" presents no special problem to the user. Normal amounts of scrap (up to about 10 pounds at a time) are often incinerated along with general plant refuse. The incinerator should have sufficient draft to exhaust all combustion products to the stack. Normal care should be taken to avoid breathing smoke and fumes from any fire. In addition, since many polymers produce acids in their combustion products ("Teflon" produces HF), the stack should be high enough to dilute the acid content of the exhaust

gases to an acceptable level. HF causes strong eye and nose irritation before approaching systemically toxic levels.[20] In addition, vegetation is particularly sensitive to HF. Where desirable vegetation is present, do not burn scrap "Teflon" in an open dump during periods of heavy humidity, fog, or smog.

Because "Teflon" resins are nonflammable, complete incineration requires sustained high temperatures from external fuel. For this reason, it is often best to dispose of scrap "Teflon" in a land-fill dump.

In the reclamation of metals by melting of scrap, it is advisable first to remove any nonmetallic components in order to avoid generating more organic vapors than necessary. In this respect, it is unnecessary to distinguish between "Teflon" resins and other polymers, since the relative hazards of breathing the combustion products are about the same in most cases. The furnace should have sufficient draft to exhaust all gases to the stack.

A question is occasionally raised concerning the storage of "Teflon" with respect to fire hazards. In most situations, whether in storage or use, the quantity of "Teflon" involved is so small in proportion to other materials that its presence is unlikely to add appreciably to the other hazards attendant to a fire. Bulk quantities of "Teflon" fluorocarbon resins and other polymers (over 100 pounds) should be stored away from flammable materials.

In the event of fire, personnel entering the storage area should use a fresh air supply, or a respirator effective against acid fumes and finely divided particulate matter. Protective clothing is also recommended to minimize contact with the skin. This type of equipment is standard in fighting many types of fires. All types of chemical extinguishers may be used to fight fires involving "Teflon", owing to its chemical inertness. Large quantities of water may also be used to cool and extinguish the fire.

II. "TEFLON" AT ORDINARY TEMPERATURES

Experiments with laboratory animals provide a means of measuring and comparing the relative toxicity of various chemicals. The extent of safe-handling procedures warranted is determined by such tests. This is usually supplemented by actual field experience.

Animal studies have shown the newer "Teflon" FEP resins to be equivalent in all important respects to "Teflon" TFE resins. For practical purposes, therefore, the following information will apply equally to the TFE and FEP products.

Animal tests clearly indicate that the resins may be taken in food without ill effect, and further, that the resins are nonirritating and nonsensitizing to the skin. In addition, there have been no known instances of dermatitis, allergy, or other ill effects in man caused by handling unheated fabricated forms of "Teflon" resins. Fabricated forms of "Teflon" resins are physiologically inert. Dust generated by grinding the unheated resins is also inert. In this respect, "Teflon" TFE and FEP resins were accepted by the U.S. Food and Drug Administration under the 1958 Food Additives Amendment as safe for contact with food during processing and cooking. They meet the requirements of FDA regulation 121.2555 for fluorocarbon resins.[15] TFE resins have been approved by the United States Department of Agriculture for use in contact with edible poultry products, in meat handling, and in cooking equipment.[16] The National Sanitation Foundation has tested "Teflon" TFE resins and found them satisfactory for potable water supply use or drain, waste, and vent systems.[17] Further statements attesting to the safety of "Teflon" resins in food uses appear in the Food and Drug Quarterly[13], the Hygienic Guide Series of the American Industrial Hygiene Association[14], and the Archives of Environmental Health.[3]

III. STABILITY TOWARD METALS AND REACTIVE CHEMICALS

The stability of "Teflon" resins with respect to various metals has been studied in some detail. It is commonly used to coat iron, steel, stainless steel, aluminum, copper, and titanium in a wide variety of applications without hazard.

"Teflon" resins react, however, with alkali metals such as sodium and potassium. This reaction serves as the basis for treatment of sheets and films to render them cementable. Furthermore, "Teflon" resins can react at elevated temperatures with certain metals when both are in a finely divided state. Thus, powdered magnesium or aluminum when mixed with finely divided "Teflon" resins can react at temperatures above 425°C (796°F). This type of reaction serves as the basis for producing a number of explosive devices used by the military. Preparation of such mixtures should be carried out only under supervision of experts trained in these highly specialized areas.

"Teflon" can react with certain strong fluorinating agents such as elemental fluorine and chlorine trifluoride. A detailed summary of the performance of "Teflon" in chemical service is available on request.[19]

IV. MEDICAL APPLICATIONS

"Teflon" resins are finding ever-increasing application in the medical field in transport of fluids, implants, and accessory equipment in hospital devices. While Du Pont has carried out tests involving the more usual applications of "Teflon", it has done little work specifically designed to determine suitability or safety in medical areas.

In examining the medical literature, one finds that "Teflon" implants have been successfully used in heart

valves, hip joints, knee joints, jaw bones, arteries, bile ducts, windpipes, and corneas. The medical profession has done and is doing an excellent job in this area. Du Pont can accept neither credit nor responsibility for the benefits or consequences of these endeavors.

It is recommended that the judgment of the medical profession be relied upon as to the suitability and safety of "Teflon" in any of the many specific medical applications where "Teflon" could be utilized.

V. SUMMARY OF APPLICATIONS

To illustrate the wide range of use of "Teflon" fluorocarbon resins a list of typical applications is presented:

1. Chemical transfer tubing
2. Fuel and hydraulic hose
3. Spaghetti tubing
4. Pipe lining
5. Bellows
6. Vessel linings
7. Films
8. Thread seal tapes
9. Cookware coatings
10. Tool coatings
11. Insulation for electrical wiring
12. Feed through and standoff terminals
13. Microwave components
14. Printed circuits
15. Bearings
16. Bearing pads
17. Seals
18. Packings
19. Piston rings
20. Gaskets
21. Conveyer belting
22. Filters
23. Laboratory ware
24. Pyrotechnics
25. Prosthetics

VI. REFERENCES

1. Lewis, E. E. and Naylor, M. A., J. Am. Chem. Soc. **69** 1968 1967.
2. Clayton, J. W., J. Occupational Med. **4** 262, 1962.
3. Zapp, J. A., Arch Environmental Health **4** 335, 1962.
4. Clayton, J. W. Fluorine Chemistry Rev. **1**(2) 197-252 1967.
5. Waritz, R. S. and Kwon, B. K. Am. Ind. Hyg. Assoc. J. **28** 19 1968.
6. Wagner, W. D. Letter Report to Res. & Techn. Serv. Br., P.H.S. Aug. 1961.
7. Kupel, R. E. and Scheel, L. D. Am. Ind. Hyg. Assoc. J. **29** 27 1968.
8. Coleman, W. E., Scheel, L. D., Kupel, R. E. and Larkin, R. L. Am. Ind. Hyg. Assoc. J. **29** 33, 1968.
9. Scheel, L. D., Lane, W. C. and Coleman, W. E., Am. Ind. Hyg. Association J. **29** 41, 1968.
10. Scheel, L. D., McMilland, L. and Phipps, F. C., Am. Ind. Hyg. Assn. J. **29**, 49, 1968.
11. Coleman, W. E., Scheel, L. D., and Gorski, C. H., Am. Ind. Hyg. Assn., J. **29**, 54, 1968.
12. Truffert, L., Am. Fals, Frandis **51** 319 1958.
13. Lehman, A. J., Assoc. Food Drug Officials U.S. Quart Bull. **26** 109, 1962.
14. Hygienic Guide Series Am. Ind. Hyg. Assn., p. 198, 1963.
15. Federal Register 121.2555 Title 21, Chap. 1. Sub Chap B, part 121, Sub part F, Oct. 13, 1962.
16. Letters,; USDA to E. I. du Pont de Nemours & Co. Aug. 26, and Sept. 29, 1964.
17. 1968 Listing of Plastic Materials, etc., p. 10, March 1968. National Sanitation Foundation.
18. Harris, D. K., Lancet **261** 1008 Dec. 1951.
19. E. I. du Pont de Nemours & Co., J. of Teflon, Vol. 11 No. 1, p. 8, 1970.
20. American Industrial Hygiene Associate Quarterly **17** p. 98 1956.

E. I. DU PONT DE NEMOURS & CO. (INC.)
POLYMER PRODUCTS DEPARTMENT
FLUOROPOLYMERS DIVISION
WILMINGTON, DELAWARE 19898

Sales Offices:

Concord Plaza
Talley Bldg.
Wilmington,DE 19898
(302) 772-5800

7250 N. Cicero Ave.
Lincolnwood
Chicago, IL 60646
(312) 982-4058

80 Universal City Plaza
Suite 400
P.O. Box 8950
Universal City, CA 91608
(213) 985-8660

IN EUROPE
Du Pont de Nemours
International, S.A.
P.O. Box CH-1211
Geneva 24, Switzerland

DUPONT

A-72531 (1/80)

Printed in U.S.A.

Produced by Saint-Gobain Performance Plastics Inc.